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## Bidisperse polymeric mixtures for independent control of viscosity and elasticity

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**Abstract** It is known that the zero shear viscosity of a polydisperse melt of linear polymers depends only on its weight-average molecular weight, whereas its recoverable compliance increases with polydispersity. These facts can be exploited to design model viscoelastic fluids using mixtures of short and long chains of the same homopolymer (bidisperse mixtures). The composition required to obtain a bidisperse mixture with the desired viscosity can be calculated from the molecular weights of the components, and the known relationship between viscosity and weight-average molecular weight. The terminal viscoelastic properties of such a bidisperse mixture are estimated from theoretical predictions for the compliance of bidisperse mixtures available in the literature. These predictions suggest that the elasticity of bidisperse mixtures can be varied independent of

their viscosity by appropriately choosing the molecular weights of their components and their composition. This strategy is applied here on bidisperse mixtures of monodisperse 1,4-polyisoprene, which are shown to display second-order fluid behavior over a reasonable range of accessible shear rates. The same procedure is also applied to mixtures of PDMS polymers which are not particularly monodisperse. Rheological measurements show that the elasticity of these polyisoprene and PDMS mixtures can indeed be varied without changing their viscosity. Such materials are ideally suited to study structure-rheological properties relationships in blends of immiscible viscoelastic fluids.

**Keywords** Bidisperse mixtures · Viscoelasticity · Model viscoelastic fluids · Immiscible blends · Boger fluids

### Introduction

Polymeric fluids show complicated rheological properties such as normal stresses, shear-thinning, time-dependence, etc. In order to understand clearly the contributions of these various aspects of complex viscoelastic behavior under given flow conditions, it is often convenient to perform research on simpler model fluids that show only some of these features, excluding others. Perhaps the best example of model viscoelastic liquids are Boger fluids which generally show strong

normal stresses in shear flow, but no other complexities (Boger 1977, 1985; Prilutski et al. 1983). Boger fluids are dilute solutions of high-molecular weight polymers, generally below the overlap concentration of the polymer coils. Relaxation of individual polymer molecules during and after deformation provides memory effects, thereby causing viscoelasticity. Due to their relatively low viscosity, transparency, and low cost, Boger fluids have proved enormously popular for studying viscoelastic phenomena (Boger and Yeow 1992).

There are, however, some experimental situations where Boger fluids are not suitable as model viscoelastic fluids. One example is the coupling between structure and rheological properties in blends of immiscible polymers. Droplet-matrix type blends composed of immiscible Newtonian fluids have been studied in great detail in recent years and there is now substantial understanding of their structure-rheology relationships (Vinckier et al. 1996; Maffettone and Minale 1998; Yamane et al. 1998; Grizzuti et al. 2000). It is of interest to extend this research to blends of immiscible viscoelastic fluids since these are of greater relevance to industrial blending operations, which often involve highly elastic polymeric melts.

At least three problems are anticipated if blends of immiscible Boger fluids are used as simple analogs of immiscible polymeric blends. First, solvents are often partially miscible, and therefore the properties of the phases and the interfacial tension are expected to change as the phases exchange solvents. Second, large polymeric molecules are known to avoid proximity to an interface to avoid loss of conformational entropy (de Gennes 1979), as well as migrate under the influence of flow (Agarwal et al. 1994). Therefore the polymer concentration in the bulk, and hence the viscoelastic properties of the bulk, are expected to differ from those close to the interface. Immiscible polymer blends typically have a large amount of surface area per unit volume due to their small-scale microstructure, and hence the effects of differences in properties between the fluid in the bulk and at the interface may be significant. Finally, on a molecular level, a Boger fluid is of course very different from a polymer melt and it is unclear as to how far the conclusions based on blends of immiscible Boger fluids may be extrapolated to blends of immiscible polymeric melts. For all these reasons, it is of interest to develop new model viscoelastic fluids that are suitable to study the effects of component viscoelasticity on the dynamics of immiscible blends. The important properties desirable for such model viscoelastic liquids are:

1. The ability to tune normal stresses without affecting the viscosity, so that the effects of changing elasticity can be clearly distinguished from those of changing viscosity
2. Substantial normal stresses in steady shear without shear thinning or equivalently, a single dominant relaxation time in the linear viscoelastic frequency spectrum
3. Viscosity between 50 and 2000 Pa.s at room temperature for experimental convenience
4. Transparency, to permit rheo-optical experiments and optical microscopy

The first point above is especially important when studying blends of immiscible liquids since the viscosity

ratio (ratio of viscosities of the immiscible phases) is known to have a large effect on the blend properties. Thus, effects of changing elasticity of the phases are likely to be obscured by concurrent changes in viscosity ratio. While increasing elasticity of a polymeric melt is rather simple (increase the molecular weight for example), doing so without affecting the viscosity is much more difficult. A rational strategy for satisfying the above criteria is evaluated in this paper.

### Theory of elasticity control with bidisperse mixtures

All polymer melts have a wide range of relaxation times and show shear-thinning at sufficiently high deformation rates. In order to be useful as model viscoelastic fluids, experiments must therefore be restricted to the terminal region which can always be described in terms of two parameters: the terminal viscosity  $\eta$ , and the longest relaxation time  $\tau$ , such that (Macosko 1994)

$$N_1 = \psi_1 \dot{\gamma}^2 = 2\eta\tau\dot{\gamma}^2; \quad J_e^0 = \frac{\tau}{\eta} \quad (1a)$$

where  $\dot{\gamma}$  is the shear rate,  $\psi_1$  the normal stress coefficient for the first normal stress difference  $N_1$ , and  $J_e^0$  is the low-shear rate or recoverable creep compliance.

In addition, the low frequency response is approximately described by the Maxwell relations:

$$G'' = \frac{\eta\omega}{1 + \omega^2\tau^2}; \quad G' = \frac{\eta\omega^2\tau}{1 + \omega^2\tau^2}; \quad \eta^* = \frac{\eta}{\sqrt{1 + \omega^2\tau^2}} \quad (1b)$$

where  $G'$ ,  $G''$ , and  $\eta^*$  are the dynamic storage modulus, loss modulus, and viscosity respectively, and  $\omega$  is the frequency. Second-order fluids obey Eqs. (1a) and (1b) at low frequencies and shear rates (Macosko 1994). Clearly, independent control of viscosity and elasticity is equivalent to changing  $\tau$ , and hence  $J_e^0$  and  $\psi_1$ , at fixed  $\eta$ . It has been observed that the zero shear viscosity of a polydisperse melt depends approximately on the weight-average molecular weight ( $\overline{M}_w$ ) alone, whereas the compliance  $J_e^0$  increases strongly with polydispersity (Masuda et al. 1970; Montfort 1976; Ferry 1980; Struglinski and Graessley 1985). This suggests that samples with the same  $\overline{M}_w$  but different polydispersity would have the same terminal viscosity but different elasticity. This idea is the basis of the present work.

The simplest case of polydispersity is a mixture<sup>1</sup> of homopolymers of just two different molecular weights. Experiments (Montfort 1976; Struglinski and Graessley 1985; Watanabe et al. 1985a; Kornfield et al. 1989) on such bidisperse mixtures have helped refine theories of

<sup>1</sup>In this paper, the term "mixture" denotes a single-phase homopolymer system containing more than one molecular weight. The term "blend" denotes a system composed of thermodynamically immiscible polymers.

dynamics of entangled melts. For such a mixture of two monodisperse, entangled, linear homopolymers it is known that (Masuda et al. 1970; Montfort 1976; Ferry 1980; Struglinski and Graessley 1985)

$$\eta_m \approx k(\overline{M_w})^\alpha = k(\phi_S M_S + \phi_L M_L)^\alpha = (\phi_S \eta_S^{1/\alpha} + \phi_L \eta_L^{1/\alpha})^\alpha \quad (2)$$

$$J_{e,S}^0 \approx J_{e,L}^0 \leq J_{e,m}^0 \quad (3)$$

where the subscripts S, L, and m stand for short chains, long chains, and mixture respectively, and  $\phi$  and  $M$  denote volume fraction and molecular weight.  $k$  and  $\alpha$  are the parameters of the viscosity-molecular weight relationship for the monodisperse homopolymers. For the case of entangled, linear polymers considered here,  $\alpha \approx 3.4$ . Equation (2) is known to overestimate the experimental viscosities of bidisperse mixtures if  $M_L/M_S \gg 1$  and  $\phi_L$  is very small (Montfort et al. 1984; Watanabe and Kotaka 1984; Watanabe et al. 1985b). For all the mixtures considered here  $M_L/M_S < 5$  and  $\phi_L > 0.08$ , and hence Eq. (2) is expected to be a good approximation. Equation (3) implies that a plot of the compliance of a bidisperse mixture as a function of  $\phi_L$  shows a maximum at some  $0 < \phi_L < 1$  (Masuda et al. 1970; Montfort 1976; Ferry 1980; Struglinski and Graessley 1985).

As mentioned above, it is the purpose of this work to make bidisperse mixtures with the same  $\overline{M_w}$ , or viscosity, but different polydispersity. Parameters of choice are the molecular weights of the short and long chains and the viscosity  $\eta_m$  of the bidisperse mixture. Once these are chosen, Eq. (2) may be inverted to find the  $\phi_L$  required to obtain the desired  $\eta_m$ :

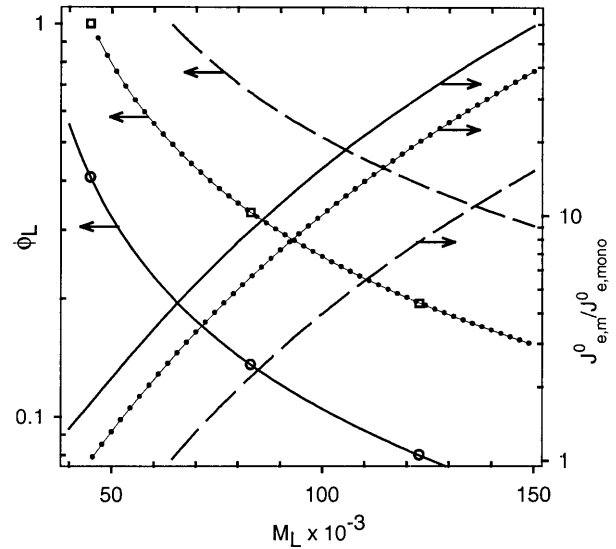
$$\phi_L = \frac{(\eta_m/k)^{1/\alpha} - M_S}{M_L - M_S} \quad (4)$$

Various theoretical and empirical expressions have been discussed by Struglinski and Graessley (1985; Graessley and Struglinski 1986) to estimate the elasticity of such a bidisperse mixture. The expression for the compliance  $J_{e,m}^0$  given by Montfort et al. (1978) which has proven successful previously (Montfort et al. 1978; Struglinski and Graessley 1985) is chosen here:

$$\frac{J_{e,m}^0}{J_{e,mono}^0} = \frac{\phi_L (M_L)^{\alpha+1} + \phi_S (M_S)^{\alpha+1}}{(\phi_L M_L + \phi_S M_S)^{\alpha+1}} \quad (5)$$

where  $J_{e,mono}^0$  is the compliance of the monodisperse, entangled polymer (independent of molecular weight). Other terminal properties such as the normal stress coefficient  $\psi_1$  and the terminal relaxation time  $\tau$  can be obtained by calculating  $J_{e,m}^0$  from Eq. (5) and substituting the result in Eqs. (1a) and (1b).

Figure 1 illustrates the qualitative features of Eqs. (4) and (5) using the  $k$  and  $\alpha$  for 1,4-polyisoprene known



**Fig. 1** Schematic of the strategy for tunable elasticity in bidisperse mixtures.  $\phi_L$  required (Eq. 4) to obtain  $\eta_m = 500$  Pa.s (solid lines),  $\eta_m = 1400$  Pa.s (dotted lines), and  $\eta_m = 5000$  Pa.s (dashed lines) using bidisperse mixtures of 1,4-polyisoprene with  $M_S = 26,000$ . The corresponding compliances are predicted using Eq. (5). The open circles and open squares are the compositions of the 1500 and 11400 series respectively employed in this work

from the viscosity-molecular weight relationship (Gotro and Graessley 1984):

$$\eta = kM^\alpha = 2.77 \times 10^{-14} M^{3.59} \text{ Pa.s at } 23^\circ \text{C} \quad (6)$$

Calculations have been performed with  $M_S = 26,000$ , for three different mixture viscosities: 5000 Pa.s, 1400 Pa.s, and 500 Pa.s. These values were chosen because bidisperse mixtures of 1,4-polyisoprene based on this same  $M_S$  and the latter two viscosity values will be discussed later in this paper. Figure 1 shows the  $\phi_L$  required to obtain the desired viscosity as per Eq. (4) as a function of  $M_L$ , and the compliance of the corresponding mixtures predicted by Eq. (5). At any fixed viscosity, the compliance  $J_{e,m}^0$ , and hence the elasticity, is seen to increase strongly with increasing  $M_L$ . It should be noted that  $\phi_L$  is much larger than in Boger fluids, and that the difference between  $M_L$  and  $M_S$  is much less than in Boger fluids (in which the low-molecular weight species are solvent molecules). Therefore the effects of gradients in concentration of long chains close to interfaces are expected to be relatively mild.

What materials are likely to allow highly elastic liquids to be realized by this method? In order to answer this question, a basic understanding of the underlying molecular dynamics is useful required (Doi et al. 1987; Viovy et al. 1991); a more detailed description may be found in a recent review (Watanabe 1999). In the following, the long chains are assumed to be well-entangled, i.e.,  $M_L \gg M_e/\phi_L$ . In a pure entangled homopolymer, the terminal relaxation time is equal to

the disengagement time of the entanglements (i.e., the reptation time) denoted by  $\tau_L$  and  $\tau_S$  for the long and short chains respectively. In a bidisperse mixture there are three kinds of entanglements: those involving two short chains (SS), one short and one long chain (SL), and two long chains (LL). Since the relaxation time  $\tau_S < \tau_L$ , the SS and SL entanglements can disengage faster than the LL entanglements. The disengagement of the LL entanglements is the slowest relaxation process and thus determines the terminal relaxation time  $\tau_m$  of the bidisperse mixture.

For  $Y = M_S^3/M_e^2 M_L \gg 1$ , it is predicted (Doi et al. 1987; Viovy et al. 1991) that the LL entanglements relax by reptation of long chains just as in a homopolymer so that  $\tau_m = \tau_L$  independent of  $\phi_L$ . Hence, the terminal relaxation time is equal to the longest relaxation time possible for the bidisperse sample. For  $Y \ll 1$ , on the other hand, the prior disengagement of the SS and SL entanglements can significantly accelerate the relaxation of the LL entanglements. This process is known as constraint release. Doi et al. (1987) suggest that constraint release causes the long chains to reptate in a tube with a larger effective diameter (called ‘tube dilation’ by Doi et al., and a ‘supertube’ by Viovy et al. 1991) and predict  $\tau_m = \phi_L \tau_L$ . Viovy et al. on the other hand suggest that the tube confining the long chain itself reptates in the supertube. They predict that  $\tau_m = \tau_L$  for  $\phi_L \gg (N_e/N_S)^3$ , and  $\tau_m = \phi_L \tau_L (N_S/N_e)^3$  for  $\phi_L \ll (N_e/N_S)^3$ . Thus, although the physical mechanisms and the  $\phi_L$  at which  $\tau_m$  deviates from  $\tau_L$  is different for the two theories, both theories predict that  $\tau_m = \tau_L$  for  $Y \gg 1$ , and that  $\tau_m < \tau_L$  is possible for  $Y \ll 1$ . To return to the question at the beginning of the previous paragraph, high elasticity corresponds to a long terminal relaxation time, and hence  $Y \gg 1$  is required so that  $\tau_m = \tau_L$ . Clearly, a polymer with a low  $M_e$  is desirable in order to easily obtain samples with high elasticity at a fixed viscosity. In this paper, 1,4-polyisoprene mixtures with  $M_e = 5100$  (Fetters et al. 1994) and  $Y > 5$ , and a PDMS mixture with  $M_e = 9500$  (Fetters et al. 1994) and  $Y > 50$ , have been studied.

## Experimental

Experiments were conducted with monodisperse polyisoprene (PI) samples, and with relatively polydisperse polydimethylsiloxane (PDMS) samples. Some characteristics of these samples are shown in Table 1. <sup>1</sup>H-NMR experiments showed that the fraction of 1,4-polyisoprene groups was 0.91–0.94 in all samples. The measured glass transition temperatures (–60 to –65 °C at 10 °C/min heating rate) agree with the measured 1,4-content (Gotro and Graessley 1984). The polydimethylsiloxanes Rhodorsil v. 100000 and Rhodorsil v. 500000 (henceforth referred to as R100 and R500) were obtained from Rhodia Chemicals. The sample designated ‘PDMS gum’ was supplied by Rheometrics Scientific as a rheological standard. All these PDMS samples were verified to have low branch content.

**Table 1** Properties of pure components

	$\eta$ Pa.s 23 °C	$\tau$ ms 23 °C <sup>a</sup>	$\overline{M}_w$ from GPC	$\overline{M}_w$ from $\eta$ <sup>b</sup>	Source
LIR30	195	1.8	24,800	26,000	Kuraray Rubber Co.
LIR50	1406	10	47,000	45,000	Polymer Source
PI87	12500	72	76,600	83,000	
PI145	51500	280	111,800	123,000	
R100	107	8.3	145,000 <sup>c</sup>	138,000	Rhodia
R500	505	53	200,000 <sup>c</sup>	210,000	Rheometrics gum
PDMS	22900	1500		590,000	

<sup>a</sup>From fitting Eq. (1b) to the terminal dynamic moduli

<sup>b</sup>Using Eqs. (6) and (9)

<sup>c</sup>Polydispersity ~1.4 as per manufacturer

Bidisperse mixtures were prepared by mixing appropriate amounts of pure components in a Petri dish with a spatula. After degassing under vacuum at room temperature, samples were allowed to stand for about three to four days prior to experiment. The diffusivities published in the literature (Appel and Fleischer 1993; Fleischer and Appel 1995) for similar materials<sup>2</sup> suggest that about one day is sufficient to achieve homogeneity at the molecular level. Rheometric experiments were performed on an RMS-800 rheometer with a 25 mm diameter, 0.1 radian cone and plate geometry using a water bath to maintain sample temperature at 23.0 °C. The highest shear rate attainable was generally limited by shear fracture at the free surface of the sample. Samples PI87, PI145, and PDMS gum were found to be difficult to load in a cone and plate geometry due to their high viscosity. Therefore frequency sweep data of these samples were obtained in a 25 mm diameter parallel plate geometry.

## Results and discussion

### Viscoelastic properties of bidisperse mixtures

The viscoelastic properties of pure polyisoprenes are shown in Fig. 2, and their viscosities at low shear rates as well as their longest relaxation times are listed in Table 1. The molecular weights  $\overline{M}_w$  of the polyisoprenes may be calculated from their measured viscosities using Eq. (6). These  $\overline{M}_w$  values agree well with the GPC results for LIR30 and LIR50, but exceed the GPC values for PI87 and PI145. It is difficult to say with confidence which set of values of molecular weights is more reliable. For the present purpose, molecular weights obtained from Eq. (6) have been used to calculate  $\phi_L$  from Eq. (4). Bidisperse mixtures of two different target viscosities, 1400 Pa.s and 500 Pa.s, were prepared. The

<sup>2</sup>Polyisoprene samples used by Fleischer and Appel (1995) had lower 1,4 content, and hence are expected to have a higher  $T_g$ . These differences in  $T_g$  were accounted for when estimating the diffusivity of our samples.

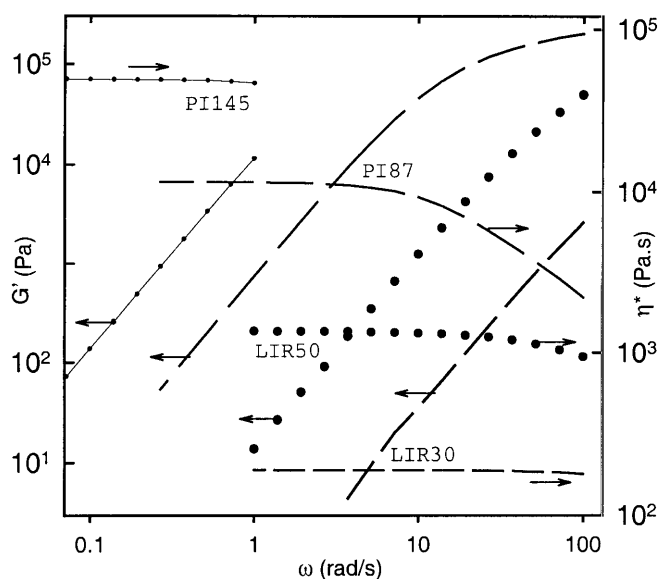


Fig. 2 Dynamic mechanical properties of pure polyisoprenes

former viscosity was chosen to match that of LIR50, whereas the latter was chosen arbitrarily. Polyisoprene mixtures are denoted with the code Ix.y where I denotes polyisoprene, x is the target viscosity in Pa.s, and y is the weight percentage of the long chain component in the sample.

The viscoelastic properties of the I1400 series are shown in Fig. 3. The equivalent plot for the I500 series is qualitatively similar to Fig. 3 and has been omitted. The terminal viscosities and normal stress coefficients of all bidisperse mixtures are summarized in Table 2. For mixtures I1400.34 and I1400.20 that contain PI87 and PI145 respectively, the measured viscosity is somewhat lower than the desired viscosity of 1400 Pa.s. The same was observed for the mixtures I500.14 and I500.08 that also contain PI87 and PI145 (see Table 2). These lower-than-expected viscosities of I1400.34, I1400.20, I500.14, and I500.08 probably occur because  $\phi_L$  was calculated using the  $M_L$  values of PI87 and PI145 obtained from their viscosities. If the GPC-derived molecular weights had been used for PI87 and PI145, Eq. (4) would have predicted a larger  $\phi_L$  for these mixtures, raising their viscosities closer to the target values of 1400 and 500 Pa.s.

The increase in  $N_1$  and  $G'$  with  $M_L$  seen in Fig. 3 demonstrates increased elasticity; Table 2 shows about a fourfold increase in  $\psi_1$  for I1400.20 as compared to the monodisperse homopolymer LIR50. This increase in  $\psi_1$  would be even larger if a slightly larger  $\phi_L$  were used to obtain  $\eta_m = 1400$  Pa.s for the bidisperse mixtures.

Thus it may be concluded from Fig. 3 that bidisperse mixtures of polyisoprenes indeed display second-order viscoelastic behavior at low shear rates, with the key

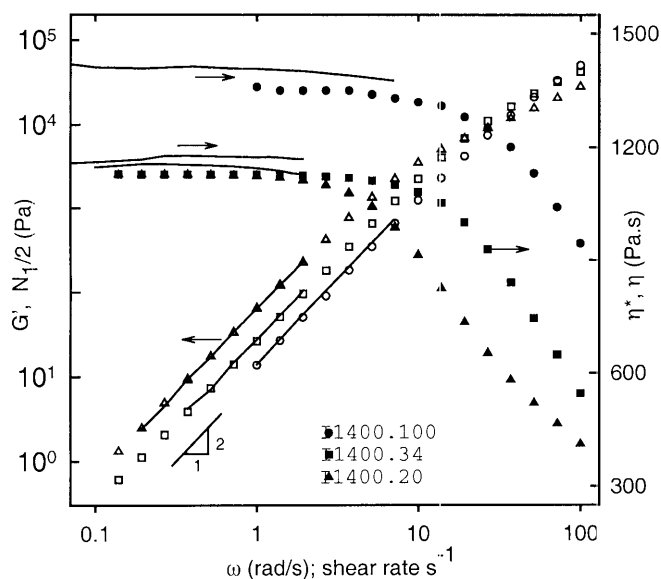


Fig. 3 Viscoelastic properties of bidisperse mixtures of polyisoprene (compositions: see Table 2). Open symbols – storage moduli  $G'$ ; solid lines superposing open symbols – steady shear  $N_1/2$ . Filled symbols – dynamic viscosities  $\eta^*$ , solid lines superposing filled symbols – steady shear viscosities  $\eta$

advantage that their elasticity can be controlled without significantly affecting their viscosity. Identical conclusions may be drawn about the I500 series (data not shown), namely elasticity increases strongly with  $M_L$  and second order behavior is observed at low shear rates.

#### Elasticity ratio of bidisperse mixtures

Assuming the Cox-Merz rule to be valid, i.e.,  $\eta(\dot{\gamma}) = \eta^*(\omega = \dot{\gamma})$ , one may use the dynamic viscosity  $\eta^*$  to estimate the shear rate ( $\dot{\gamma}_m$ ) up to which the samples may be expected to show no shear-thinning. Here  $\dot{\gamma}_m$  is defined arbitrarily as the shear rate at which the viscosity decreases to 95% of the zero-shear viscosity, i.e., the  $\omega$  at which  $\eta^*$  reaches 95% of its terminal value. These values of  $\dot{\gamma}_m$  are tabulated in Table 2. One measure of the elasticity of a viscoelastic fluid is the elasticity ratio E:

$$E(\dot{\gamma}) = \frac{\text{normal stress } N_1}{\text{shear stress } \eta \dot{\gamma}} = \frac{\psi_1 \dot{\gamma}}{\eta} \quad (7)$$

Table 2 shows that the maximum E obtainable for the mixtures without shear-thinning,  $E(\dot{\gamma}_m)$ , is about 0.4 for all samples. This value is considerably lower than the values attainable for Boger fluids, which can easily reach  $E=10$  without shear thinning (Boger 1977, 1985; Prilutski et al. 1983), i.e., the present samples are far less elastic than Boger fluids. The reason for this may be

**Table 2** Properties of bidisperse mixtures

Sample designation	Short component	Long component	$\phi_L$	$\eta$ Pa.s 23 °C	$\tau_m$ ms 23 °C <sup>a</sup>	$\psi_1$ Pa.s <sup>2</sup>	$\dot{\gamma}_m$ s <sup>-1b</sup>	$E(\dot{\gamma}_m)$
I1400.100	None	LIR50	1.0	1406	8.3	29.3	20	0.42
I1400.34	LIR30	PI87	0.34	1176	25	55.3	10	0.47
I1400.20	LIR30	PI145	0.20	1151	58	125	3.7	0.40
I500.41	LIR30	LIR50	0.41	520	5.7	5.8	37	0.41
I500.14	LIR30	PI87	0.14	471	12	9.4	20	0.40
I500.08	LIR30	PI145	0.085	427	24	19.1	8	0.36
S500.100	None	R500	1.0	505	53	45.8	3.6	0.33
S500.16	R100	PDMS gum	0.16	520		<sup>c</sup>	0.5	

<sup>a</sup>From fitting Eq. (1b) to the terminal dynamic moduli

<sup>b</sup>Estimate of the  $\dot{\gamma}$  up to which constant  $\eta$  may be expected (see section ‘Elasticity ratio of bidisperse mixtures’)

<sup>c</sup> $\log(N_1)$  vs.  $\log(\dot{\gamma})$  has slope 1.6

understood by estimating the maximum  $E$  for a second-order fluid. As per Eq. (1b),  $\eta^*/\eta = 0.95$  at  $\omega\tau = 0.33$ . Then assuming  $\eta(\dot{\gamma}) = \eta^*(\omega = \dot{\gamma})$  and  $N_1(\dot{\gamma}) = 2G'(\omega = \dot{\gamma})$ , Eqs. (1) and (7) predict  $E = 0.63$  as the maximum elasticity ratio obtainable from a second-order fluid with no more than 5% shear-thinning. The value of 0.4 obtained for the bidisperse blends is comparable to this maximum value for a second-order fluid. Thus it appears that in any fluid that behaves similar to a second-order fluid, i.e., has a single dominant relaxation time,  $E$  will not exceed  $O(1)$  without substantial shear thinning, because the same physical process that causes normal stresses is also responsible shear thinning.

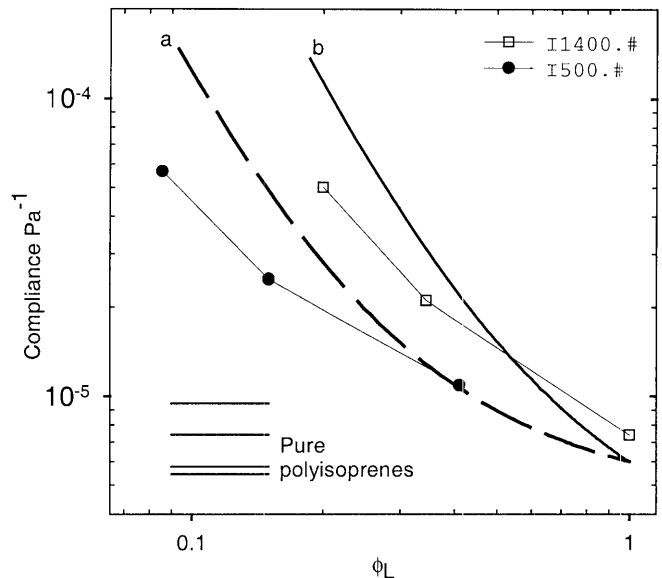
### Compliance and terminal relaxation time

Figure 4 plots the compliance of all samples, calculated using

$$J_e^0 = \lim_{\omega \rightarrow 0} \frac{G'}{G''^2} \quad (8)$$

as a function of  $\phi_L$ . These compliances have been compared with the prediction of Montfort et al. (1978) (Eq. 5) on which Fig. 1 is based.  $J_{e,mono}^0 = 6 \times 10^{-6} \text{Pa}^{-1}$  has been used for monodisperse polyisoprene (Gotro and Graessley 1984) in this calculation. It is found that Eq. (5) predicts the correct trends, but generally overestimates the compliance. As such, when formulating bidisperse mixtures for specific purposes, Eq. (5) is suitable only for obtaining a rough estimate of the elasticity.

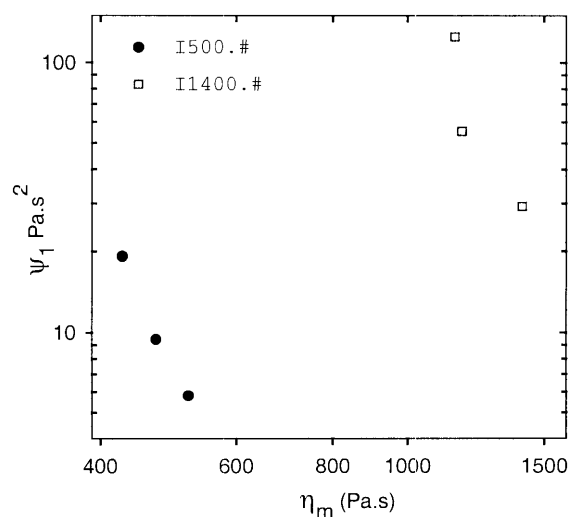
The terminal relaxation times  $\tau_m$  of the samples, obtained by fitting the low-frequency dynamic moduli to Eq. (1b), are listed in Table 2. It is found that  $\tau_m$ , like the compliance, increases with polydispersity. A comparison of the  $\tau_m$  with the  $\tau_L$  values for the long chains of the bidisperse mixtures from Table 1 reveals that  $\tau_m \ll \tau_L$ . Thus, for example, for the I1400.20 sample for which  $Y = M_3^2/M_c^2 M_L = 5.5$ ,  $\tau_m = 58$  ms, whereas



**Fig. 4** Compliance of bidisperse mixtures. The four horizontal lines are the compliances of pure components: PI145, PI87, LIR50, and LIR30 in increasing order. The Montfort et al. predictions (dashed line ‘a’ for 500 Pa.s and solid line ‘b’ for 1400 Pa.s) were obtained by substituting Eq. (4) into Eq. (5)

$\tau_L = 280$  ms. This is somewhat surprising since, as mentioned previously in the paper, for  $Y \gg 1$ ,  $\tau_m = \tau_L$  has been predicted (Doi et al. 1987; Viovy et al. 1991) and observed experimentally (Struglinski and Graessley 1985; Kornfield et al. 1989). Indeed, the polyisoprene samples were chosen for experiments with the expectation that with  $Y \gg 1$ ,  $\tau_m = \tau_L$  could be obtained. The most likely explanation for this is that the compliance of the short chain component of the mixtures, LIR30, is much higher than of the other pure polyisoprenes, as seen in Fig. 4. This suggests that LIR30 is not well-entangled, violating an important assumption of the theories.

The success of elasticity control in bidisperse mixtures of polyisoprene is summarized in Fig. 5,



**Fig. 5** Summary of elasticity control at fixed viscosity using bidisperse mixtures with compositions noted in Table 2

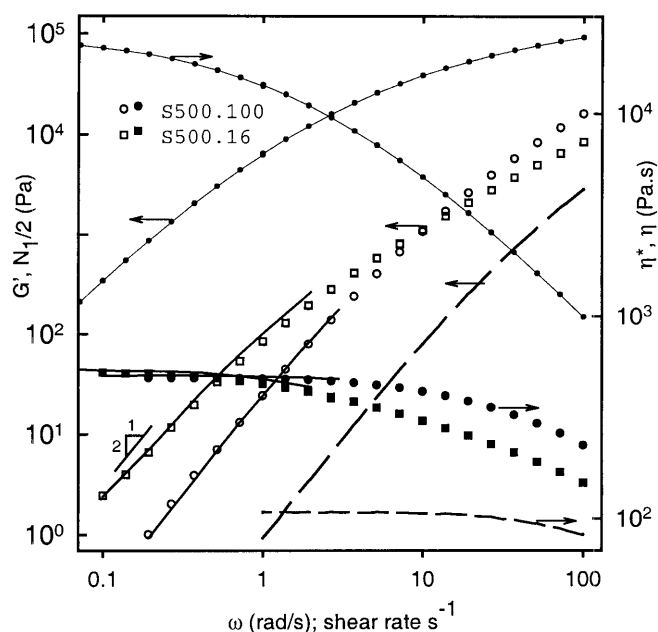
where the increasing first normal stress coefficient with relatively little change in viscosity is seen clearly. We reiterate that the lower viscosity of the mixtures I1400.34, I1400.20, I500.14, and I500.08 can be attributed to the use of somewhat incorrect values of molecular weights of PI87 and PI145 in Eq. (4). The viscosities of these mixtures can be raised to the target value by simply increasing their  $\phi_L$  slightly. This would make the trend of increasing elasticity in Fig. 5 even more obvious.

#### Elasticity control with polydisperse PDMS mixtures

The polyisoprene mixtures discussed so far were composed of monodisperse samples which are, in general, not easily available. It is therefore of interest to examine whether the same control over elasticity may be exerted using mixtures of polydisperse commercial polymers. The PDMS samples in Table 1 were chosen for this purpose. The molecular weights of the components were calculated using the measured viscosities and the known relationship (Dvornic 1996) between molecular weight and viscosity:

$$\eta = 1.3 \times 10^{-17} M^{3.68} \text{ Pa.s at } 23^\circ\text{C} \quad (9)$$

The R500 sample, which has a viscosity of 505 Pa.s at 23 °C, is designated S500.100 (following the convention Sx.y where S denotes silicone, x, the viscosity in Pa.s, and y the weight fraction of long chains). Equation (4) predicts that the same viscosity of 505 Pa.s can be obtained by mixing 16 wt% of the PDMS gum with R100. Table 2 confirms that the viscosity of this “bidisperse” sample, which is designated S500.16, is indeed close to that of S500.100. Figure 6 shows the



**Fig. 6** Viscoelastic properties of PDMS samples. *Open symbols* – storage moduli  $G'$ ; *solid lines superposing open symbols* – steady shear  $N_1/2$ . *Filled symbols* – dynamic viscosities  $\eta^*$ , *solid lines superposing filled symbols* – steady shear viscosities  $\eta$ . Pure component  $G'$  and  $\eta^*$  are shown for PDMS gum (*dotted lines*) and R100 (*dashed lines*)

properties of S500.100 and S500.16, along with the dynamic properties of the pure components PDMS gum and R100 that constitute S500.16. The larger  $N_1$  and  $G'$  of S500.16 as compared to S500.100 confirm increased elasticity of S500.16, and the agreement between  $N_1/2$  and  $G'$  is satisfactory. However in contrast with the polyisoprene mixtures:

1.  $G' \propto \omega^2$  and  $N_1 \propto \dot{\gamma}^2$  is not observed at low  $\omega$  or  $\dot{\gamma}$  for S500.16, i.e., neither the terminal zone of the dynamic moduli nor the second order region of the steady state data could be reached experimentally for S500.16.
2. The “bidisperse” S500.16 sample is expected to become shear-thinning at a relatively low shear rate ( $\eta^*$  drops to 95% of its terminal value at a frequency of about 0.5 rad/s)

Thus, while monodisperse components are not essential for elasticity control, one may generally expect relatively complex rheological behavior from mixtures of more polydisperse components. As such, they may be suitable for qualitative experiments only.

#### Summary and conclusions

This paper demonstrates the use of a rational procedure for controlling the elasticity at constant viscosity of polymeric melts by means of bidisperse mixtures of entangled monodisperse polymers. Experiments with

1,4-polyisoprene show that increasing the length of the longer chains, while keeping the shorter chain unchanged, causes a significant increase in the first normal stress coefficient without significant change in viscosity. The resulting mixtures were found to have an accessible terminal zone at low frequencies and a second order region at low shear rates. Normal stresses of up to 40% of the shear stresses could be achieved without shear-thinning. While the facts that the compliance of polymer melts increases with polydispersity, and that constraint release is responsible for this phenomenon have been known for several decades (Masuda et al. 1970), this result has not been applied to realize fluids with tunable elasticity prior to this work.

The key difference between Boger fluids and the present bidisperse materials is that viscoelasticity is controlled by deformation and relaxation of single chains in the former, but by constraint release of entangled, reptating chains in the latter. Some of the advantages expected of using bidisperse mixtures, rather than Boger fluids, as model viscoelastic phases of immiscible blends are:

1. The bidisperse mixtures do not contain any solvents or low molecular weight species. Hence phenomena such as solvent evaporation or exchange of solvent between phases are not complicating factors when performing experiments.
2. The low frequency and low shear rate behavior of the present materials can be well-represented by a

second-order fluid. This is expected to simplify interpretation of experiments, for example, comparison between stress relaxation and dynamic oscillatory experiments. This is unlike some Boger fluids for which  $N_1(\dot{\gamma}) \gg 2G'(\omega = \dot{\gamma})$  has been found (Prilutski et al. 1983).

3. The bidisperse mixtures described here are far less polydisperse as compared to Boger fluids; hence, gradients in concentration of long chains are not expected to be as severe in bidisperse mixtures. In addition, at least one key property of blends of highly immiscible polymer melts, namely interfacial tension, is almost independent of molecular weight and is unaffected by concentration gradients.
4. Finally, on a molecular level, commercial polymeric melts are better represented by bidisperse mixtures of the kind discussed here, than by Boger fluids.

The primary disadvantage of bidisperse mixtures, or indeed any fluid with a single dominant relaxation time, is that the elasticity ratio attainable without shear-thinning is considerably lower than that attainable from Boger fluids.

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